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## II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE, UNDER THE DIRECTION OF  
PROFESSOR JOSIAH P. COOKE.

DOUBLE HALOID SALTS OF ANTIMONY, CALCIUM,  
AND MAGNESIUM, WITH OBSERVATIONS ON  
THE REMARKABLE DISSOCIATION OF  
THESE COMPOUNDS.

BY FRANCIS GANO BENEDICT, A. M.

Presented by J. P. Cooke, May 9, 1894.

IN a recent paper,\* we described the results of our study of the double haloids of antimony and the alkaline metals. Since then we have extended the investigation to the corresponding compounds with calcium and magnesium, and, although the work is still in an unfinished state, it must necessarily be interrupted for the present; and we therefore give here the results thus far obtained, the most important of which is *the complete dissociation of a definite crystalline salt at the ordinary temperature of the air.*

In the paper referred to,† a salt was mentioned having the composition  $\text{SbCl}_3 \cdot 2 \text{KCl} \cdot 2 \text{H}_2\text{O}$ , and the difficulties encountered in its preparation, analysis, and crystallographic study were discussed. Chief among these difficulties was the circumstance that the water of crystallization was lost wholly or in part at temperatures above  $-5^\circ$  Cent., requiring the salt to be handled in a room below that temperature. In dealing with these new compounds the necessity for cold weather is even greater than in the case just mentioned. Hence the advancing of the season has prevented further work on this line. The research will be continued at the earliest opportunity.

Poggiale,‡ in 1845, was the first investigator to obtain double haloids of antimony and the earthy alkaline metals: "Le chlorure de barium, uni au chlorure d'antimoine, présente une particularité qui

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\* These Proceedings, XXIX. 212.

† Comptes Rendus, XX. 1180.

‡ *Loc. cit.*

mérite d'être mentionnée. Si la solution de chlorure de barium n'est pas concentrée les deux sels séparent par le refroidissement; le chlorure de barium cristallise en tables, tandis que le protochlorure d'antimoine décompose l'eau. Il faut donc pour obtenir cette combinaison, concentrer la solution de chlorure de barium, avant d'y ajouter le protochlorure d'antimoine. La liqueur donne alors des aiguilles fines disposées en groupes étoilés. Ce sel double est composé de



Le protochlorure d'antimoine se combine également avec les chlorures de strontium, de calcium et de magnésium."

Schäffer,\* in 1860, working on the double iodides of antimony and the alkaline metals, described the double iodide of antimony and barium as a yellow salt with a formula,



Storer † gives a list of salts, viz. : —



Watts's Dictionary ‡ gives the formula alone of a salt of this class, i. e.  $2 (\text{BaCl}_2 \cdot \text{SbCl}_3) 3 \text{H}_2\text{O}$ .

Graham-Otto § makes the simple statement that antimonious chloride forms crystalline compounds with the chlorides of the alkaline and earthy alkaline metals.

Poggiale and Schäffer, therefore, appear to be the only investigators who succeeded in obtaining compounds with the earthy alkaline metals.

Although we have obtained a great many beautifully crystalline compounds from various mixtures of the haloids of antimony with the haloids of calcium, magnésium, barium, and strontium, only three of these have as yet been investigated. As has been before stated, cold weather is an absolute essential in the formation of the compounds, and the season is so far advanced that no more work can be done on them this year.

\* Pogg. Ann., CIX. 611.

† Dictionary of Solubilities, p. 149.

‡ Edition of 1888, Vol. I, p. 287.

§ Michaelis edition, Vol. II. p. 555.

The following salts have been prepared and analyzed, and the formulæ deduced for them are : —

- I.  $\text{SbCl}_3 \cdot \text{CaCl}_2 \cdot 8 \text{H}_2\text{O}$ .
- II.  $\text{SbBr}_3 \cdot \text{CaBr}_2 \cdot 8 \text{H}_2\text{O}$ .
- III.  $\text{SbBr}_3 \cdot \text{MgBr}_2 \cdot 8 \text{H}_2\text{O}$ .

The materials used in the preparation of these salts were obtained as follows. The antimonious chloride and calcic chloride were the "chemically pure" products of the market. The antimonious bromide was made by the direct union of finely powdered metallic antimony and bromine in carbon bisulphide, after the manner described by Professor Cooke.\* The calcic bromide and magnesian bromide were made by the action of pure hydrobromic acid upon pure calcic carbonate and magnesian carbonate respectively.

No difficulty was experienced in obtaining the three salts just named by mixing their components in approximately molecular proportions, adding just enough free acid to effect the complete solution of the antimony salt and evaporating the mixture in a crystallizing dish in a vacuum over sulphuric acid. Fortunately there was a room in the laboratory in which the temperature could be regulated quite easily so as to keep it at about  $0^\circ$  Cent. and not let it fall low enough to solidify the mixtures, thus offering the most favorable conditions to crystallization. The large isolated crystals were removed in the cold room, crushed in a mortar, hastily rubbed between filter papers and placed in glass-stoppered weighing bottles. Of necessity this operation required considerable dexterity to prevent any change in weight, but experience has shown that the whole operation can be performed in 45 to 50 seconds, with no appreciable change in the composition of the salt.

With but one exception the analysis of these salts presented no great difficulty.

Antimony was determined in the usual manner, by weighing as antimonious sulphide. All the precautions of this determination, as advised by Professor Cooke in his fundamental work on the atomic weight of antimony,† were closely observed.

Bromine and chlorine were determined as their respective silver salts. The presence of tartaric acid necessary for the solution of the antimony salt interferes to some extent in this determination by pre-

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\* These Proceedings, XIII. 52.

† Ibid., XIII. 1-114.

cipitating that crystalline salt "silver emetic," discovered by Wallquist\* and further studied by Professor Cooke.†

However, if care is taken to have only a slight excess of silver nitrate over the calculated amount, and to precipitate from dilute solutions, the probable error is reduced to a minimum.

Calcium was determined by igniting calcic oxalate precipitated in the usual way, and weighing as calcic oxide. This method was very satisfactory. Magnesium was weighed as magnesian pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ) formed by the ignition of the ammoniac magnesian phosphate ( $\text{NH}_4\text{MgPO}_4$ ) precipitated in the usual manner.

The presence of tartaric acid evidently interferes to some extent with the perfect working of this determination; but as the per cent of magnesium in the salt was so small the error was not prominent.

The determination of the water of crystallization presented the first serious difficulty, for, drying the salt in an air bath at  $98^\circ$ – $100^\circ$  showed rapid decomposition. In fact, no temperature was found at which the water would all go off and the salt remain undecomposed.

On placing the salt in a vacuum desiccator the loss was considerably greater than theory would require, till finally the residue amounted to but about 24% of the whole amount of salt used. Even in an ordinary desiccator there was a gradual loss in weight, and constancy was only reached when the residue was about 24% of the total mass, as before. At the suggestion of Professor Cooke the salt was intimately mixed with a quantity of ignited oxide of magnesia (heavy) in a crucible and heated to constant weight. In this operation it was necessary to get the upper layer of magnesian oxide hot before heating the lower part of the crucible containing the compound. Should any antimony haloid be volatilized, it would be decomposed upon reaching the hot layer of oxide of magnesium. This method served excellently for the first salt, i. e.  $\text{SbCl}_3 \cdot \text{CaCl}_2 \cdot 8 \text{H}_2\text{O}$ . The oxide of magnesia seemed to retain the antimonious chloride readily, but when the same process was applied to the analysis of the bromides it was found that the magnesian oxide would not retain all of the bromide of antimony. The escape of this salt was clearly observed by the color of the flame held over the mouth of the crucible.

After several trials, a modification of the apparatus described by Jannasch and Locke ‡ was decided upon as giving the most satisfac-

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\* Gmelin, Handbook, Cavendish ed., X. 326.

† These Proceedings, XVII. 5.

‡ Zeitschrift für Anorgan. Chemie, VI. 174.

tory results. For this purpose some litharge was heated to constant weight, thereby expelling all the carbonic acid gas and moisture. The weighed salt from a weighing bottle was mixed with several grams of the ignited lead oxide in a porcelain boat large enough to fit a combustion tube of two centimeters internal diameter. This was placed in a kerosene oven and dry air drawn through it. Upon heating, the water expelled was absorbed in two weighed U tubes containing sulphuric acid and phosphoric pentoxide respectively. The apparatus for drawing dry air through the combustion tube was devised, and described at length by Professor Cooke in his paper on "A New Method of Determining Gas Densities." \*

This process for determining water is an ideal one, every trace of the antimony haloid being retained, and the water passing off freely at a moderate temperature,  $250^{\circ}$ . The results were surprisingly constant.

Although these several analyses are not as concordant with theory as one would wish, yet, when the instability of the compound, the necessarily hasty drying of the salt (freeing from mother liquor), and the difficulties of purification, are taken into consideration, the results are not at all beyond a reasonable limit of error.

In all three cases we could deal with large isolated crystals. There was no case of a complex crystalline precipitate, for all three compounds are most perfectly crystalline, and the only sources of contamination are occlusions of mother liquor and imperfect drying due to the haste required in transferring the salt to the weighing bottle. All three salts are decomposed by water, and are soluble in tartaric, hydrochloric, and hydrobromic acids. The last two solvents must be somewhat concentrated, as an excess of water decomposes the antimony salt.

#### I. $\text{SbCl}_3 \cdot \text{CaCl}_2 \cdot 8 \text{H}_2\text{O}$ .

This is a beautifully crystalline salt, individual crystals often occurring over one inch in length. They are large, colorless plates, apparently belonging to the triclinic system. Their tendency to effloresce and decompose prevented any very satisfactory crystallographic examination, although traces of biaxial structure were observed with a polariscope. The salt loses all the water of crystallization and all the antimonious chloride in a desiccator over sulphuric acid, leaving a residue of nearly anhydrous calcic chloride.

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\* These Proceedings, XXIV. 213, and American Chem. Journal, XI. 521.

- a.* 0.3607 gram of salt gave 0.1259 gram of antimonious sulphide.
- b.* 0.4342 gram of salt gave 0.0526 gram of calcic oxide.
- c.* 0.2322 gram of salt gave 0.3499 gram of argentic oxide.
- d.* 1.0737 grams of salt gave 0.3154 gram of water.

	Calculated * for $\text{SbCl}_3 \cdot \text{CaCl}_2 \cdot 8 \text{H}_2\text{O}$ .	Found.
Antimony	24.95	24.93
Calcium	8.31	8.65
Chlorine	36.82	37.26
Water	29.92	29.37
	<u>100.00</u>	<u>100.21</u>

## II. $\text{SbBr}_3 \cdot \text{CaBr}_2 \cdot 8 \text{H}_2\text{O}$ .

This salt crystallizes well in large tabular crystals, often exceeding half an inch in length. Aside from the fact that the polariscope showed no interference figure, no crystallographic study of the salt could be made owing to its unstable nature. This salt, precisely as its analogue above, loses all its water of crystallization and also the antimonious bromide in a desiccator, till finally a nearly anhydrous residue of calcic bromide is left. Analysis gave the following results:—

- a.* 0.3742 gram of salt gave 0.0896 gram of antimonious sulphide.
- b.* 1.1896 grams of salt gave 0.0909 gram of calcic oxide.
- c.* 0.3090 gram of salt gave 0.4191 gram of argentic bromide.
- d.* 0.8415 gram of salt gave 0.1720 gram of water.

	Calculated for $\text{SbBr}_3 \cdot \text{CaBr}_2 \cdot 8 \text{H}_2\text{O}$ .	Found.
Antimony	17.07	17.10
Calcium	5.68	5.46
Bromine	56.79	†57.72
Water	20.47	20.44
	<u>100.00</u>	<u>100.72</u>

## III. $\text{SbBr}_3 \cdot \text{MgBr}_2 \cdot 8 \text{H}_2\text{O}$ .

This salt crystallizes very well in large well defined tabular crystals, apparently isomorphous with the preceding salt. Large well shaped

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\* Atomic weights used: Sb=120; Cl=35.456; Ca=40; H=1.0075; O=16; Br=79.955; Mg=24.36.

† This excess of 1% of Br is probably due to the fact that the substance was not perfectly freed from mother liquor rich in hydrobromic acid; approaching warm weather would not permit of purification by recrystallization.

crystals gave no interference figure with the polariscope. This salt, as the others, loses all its water of crystallization and antimonious bromide in a desiccator over sulphuric acid, leaving a residue of magnesian bromide. Analysis gave the following results:—

- a.* 0.9131 gram of salt gave 0.2193 gram of antimonious sulphide.
- b.* 1.1178 grams of salt gave 0.2128 gram of magnesian pyrophosphate.
- c.* 0.5160 gram of salt gave 0.7044 gram of argentic bromide.
- d.* 0.7013 gram of salt gave 0.1469 gram of water.

	Calculated for $\text{SbBr}_3 \cdot \text{MgBr}_2 \cdot 8 \text{H}_2\text{O}$ .	Found.
Antimony	17.40	17.15
Magnesium	3.54	4.06
Bromine	58.07	58.09
Water	20.99	20.95
	100.00	100.25

These three salts possess two important relations:—

1. Entire uniformity of structure, i. e. one molecule of the alkaline haloid combining with one molecule of the antimony haloid, and the resulting compound crystallizing in each case with eight molecules of water.

2. Each salt completely dissociates at the ordinary temperatures in a desiccator.

The most striking feature of this research is the above mentioned phenomenon. On attempting to estimate the water of crystallization by desiccation, an irritating odor first indicated a decomposition which was conclusively proven by the continual loss in weight. When constancy in weight was obtained, the residue on treating with water gave a hissing sound, and dissolved to a perfectly clear solution. This solution, on acidifying with hydrochloric acid and adding a solution of hydrogen sulphide, gave no precipitate, indicating an absence of antimony.

In the case of the salt  $\text{SbCl}_3 \cdot \text{CaCl}_2 \cdot 8 \text{H}_2\text{O}$ , the per cent of residue was 24.64, while the theoretical per cent of calcic chloride in the salt is 23.04. The excess would naturally be attributed to water which the calcic chloride would not readily yield to the sulphuric acid in the desiccator. The strong smell (volatilized antimony haloid) in the desiccator was observed long before the theoretical amount of loss calculated as water, i. e. 29.92%, had taken place. This showed that the antimony haloid had escaped before all the water had left the mass.



In the case of the double bromides, a singularly beautiful phenomenon took place. The antimonious bromide would sublime and crystallize all over the edge of the powdered mass of salt in those characteristic fine colorless needles measured and described by Professor Cooke.\* These crystals were for the most part of microscopic size, but some attained a length of two or three millimeters. On further desiccation they soon disappeared. As would be expected, a direct experiment showed that the salt  $\text{SbCl}_3 \cdot \text{CaCl}_2 \cdot 8 \text{H}_2\text{O}$  decomposed much more rapidly than the salt  $\text{SbBr}_3 \cdot \text{CaBr}_2 \cdot 8 \text{H}_2\text{O}$ , under precisely similar conditions.

Richards, † in 1890, described a tetra ammon-cupriammonium bromide with a formula  $\text{CuBr}_2 \cdot 6 \text{NH}_3$ , which loses four molecules of ammonia in a desiccator, forming  $\text{CuBr}_2 \cdot 2 \text{NH}_3$ . Although the escape of ammonia from its compounds is not uncommon, yet we believe this is the nearest case to the one in point, inasmuch as the loss here is perfectly definite.

The escape of antimony haloids from these compounds at a low temperature has a very important bearing on the question of molecular combination. It is almost universally admitted that the relation of the water of crystallization to a salt is different from that of its other components. A study of these compounds, however, shows that there is apparently no greater affinity between the two haloids than between the compound and the water of crystallization. Hence, in whatever manner the latter is combined, it is reasonable to suppose a similar union of the two haloids. If, therefore, the crystal water of a salt is held in molecular combination, the evidence as set forth in this research would be interpreted as signifying a molecular union of the two haloids.

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\* These Proceedings, XIII. 76.

† Berichte der deutsch. Chem. Gesell., XXIII. 3790.